PEER REVIEW OF THE SAPRC-07 CHEMICAL MECHANISM OF DR. WILLIAM CARTER

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SAPRC-07 Specific Sources

The SAPRC-07 mechanism and its documentation were taken from Dr. Carter's website (http://www.engr.ucr.edu/~carter/SAPRC/).

- Mechanism reviewed was "SAPRC07B Mechanism; Created from Mech07.XLS 4-Jul-2008".

- Documentation used was William P. L. Carter "Development of a Condensed SAPRC-07 Chemical Mechanism," Report to the California Air Resources Board, Contract No. 05-750, July 4, 2008.

Methodology – 1

Compare species between SAPRC-07, CB05 and RACM2

SAPRC		CB05		RACM2	
ALK1	Primarily ethane	ETHA	Ethane	ETH	ethane
ALK2	Primarily propane	PAR	Paraffin carbon bond	HC3	kHO <3.4x10^{-12} cm^3 s^{-1}
ALK3	Alkanes with kOH between 2.5 x 10^3 and 5 x 10^3 ppm^{-1} min^{-1}	PAR	Paraffin carbon bond	HC5	kHO between 3.4x10^{-12} to 6.8x10^{-12} cm^3 s^{-1}
ALK4	Alkanes with kOH between 5 x 10^3 and 1 x 10^4 ppm^{-1} min^{-1}	PAR	Paraffin carbon bond		
ALK5	Alkanes with kOH greater than 1 x 10^4 ppm^{-1} min^{-1}	PAR	Paraffin carbon bond	HC8	kOH > 6.8x10^{-12} cm^3 s^{-1}

Methodology – 2

Compare reactions between SAPRC-07, CB05 and RACM2

SAPRC07<BR21> MECO3 + NO → MEO2 + CO2 + NO2 # 7.50e-12@-290
CB_05_R87 C2O3 + NO → MEO2 + NO2 8.1E–12 @ –270
RACM2_209 ACO3 + NO → MO2 + NO2; THERMAL A-FACT 8.10E-12 E/R -270

SAPRC07<BR22> MECO3 + HO2 → AACD + 0.3*O3 # 5.20e-13@-980
CB_05_R91 C2O3 + HO2 → 0.800*PACD + 0.200*AACD + 0.200*O3 4.3E–13 @ –1040
RACM2_233 ACO3 + HO2 → 0.4 PAA + 0.2 ORA2 + 0.4 MO2 + 0.4 HO + 0.4 CO2; THERMAL A-FACT 4.3E-13 E/R -1040.

SAPRC07<BR23> MECO3 + NO3 → MEO2 + CO2 + NO2 # 1.0*KSAPRC07<BR09>
CB_05_000 No Equivalent
RACM2_320 ACO3 + NO3 → MO2 + NO2; THERMAL A-FACT 4.00E-12 E/R 0.0

SAPRC07<BR26> MECO3 + RO2XC → AACD # 1.0*KSAPRC07<BR25>
CB_05_000 No Equivalent
RACM2_000 No Equivalent

Chemical Species

◆The number and type of chemical species in SAPRC07 appear to be consistent with the state-of-the-science.

◆The version of SAPRC07 used in this review includes 136 model species.

◆At this time the number of species in SAPRC-07 is consistent with the requirements of urban and regional photochemical models to provide an adequate level of detail consistent with currently available computational resources.

Alkene Reactions

Overall the treatment of alkenes is within the state-of-the-science in SAPRC-07.

SAPRC-07 includes the reaction of ground state oxygen atom with many alkenes. This may be a remnant of environmental chamber testing; it probably is not significant under most atmospheric conditions.

Methacrolein, Methyl Vinyl Ketone

The products of the reaction of methacrolein with HO, O3 and NO3 are very different between the three mechanisms. SAPRC-07 includes reactions for a species that represents lumped isoprene products that is not equivalent to the treatment in the other two mechanisms.

Terpene Reactions

SAPRC-07 includes only one terpene species. Differentiating α-pinenes and other cyclic terpenes with one double bond and a second species for d-limonene and other cyclic diene-terpenes could be improved in future versions of SAPRC.

Acetylene Reactions

SAPRC-07 also includes the reaction of ozone with acetylene. This is a worthwhile addition to the mechanism given that it adds no extra species to the mechanism.

Aromatic Reactions

For benzene the product yields of many species are different between the mechanisms, especially for HO2 but it is difficult to determine which approach is better given the complex nature of aromatic oxidation.

Aromatic chemistry remains very difficult to characterize due to it complexity and its many remaining scientific uncertainties. The divergence between the three mechanisms is great.

The SAPRC approach is acceptable within the current state of the science.

Dicarbonyl Reactions

There are three photolysis reactions of glyoxal: a reaction that produces HO_2 and CO; a reaction that produces HCHO and CO; and a third reaction that produces H_2 and CO.

RACM2 includes all three but SAPRC-07 omits the third.

Another concern is that for the reactions of glyoxal with HO and nitrate radical SAPRC-07 forms a higher acyl peroxy radical and a negative quantity of lost carbon. **WHY???**

This appears to offset the production of the higher acyl peroxy radical but does subtracting lost carbon add carbon to the system?

Acetaldehyde Reactions and Higher Aldehyde Reactions

SAPRC-07 produces several operator radicals while CB05 produces one operator radical and RACM2 produces a surrogate radical species. The SAPRC-07 approach may allow better treatment of some compounds that are aggregated into the RCHO species.

Reactions Involving PAN, Homologues and Acyl Peroxy Radicals

SAPRC-07 includes a higher peroxyacyl nitrate compound and an aromatic PAN like compound that are not included in CB05 and RACM2. This is a good feature because when mechanisms are simplified, much of the carbon is channeled to acetaldehyde and formaldehyde much faster than in reality. Having more of the higher aldehydes and peroxyacyl nitrate compounds helps reduce this problem.

Peroxy Radical Reactions

SAPRC-07 alone includes a direct treatment of t-butoxy radical reactions. This should help it more accurately account for the yield of organic nitrate and it might help it characterize secondary organic aerosol yields.

SAPRC-07 has its own scheme of using operators to treat peroxy radical reactions. SAPRC-07 includes a number of active peroxy radical operators and it uses the operator approach much more extensively than either CB05 or RACM2. SAPRC's approach to the treatment of peroxy radical chemistry this level of treatment is very reasonable. The SAPRC-07 operator scheme is within the state of the science.

Reactions that Could Be Eliminated

Most $O(^3P)$ Reactions

Formaldehyde Reactions

The reaction $HCHO + HO_2 \rightarrow HOCOO + H_2$ and subsequent reactions for HOCOO could be eliminated to save computational resources. Sensitivity tests made during the development of RACM2 for realistic atmospheric conditions showed that this reaction was not significant.

SAPRC-07 Chlorine Reactions

SAPRC-07 is the only one of the mechanisms with chlorine chemistry in the versions that were examined. SAPRC-07 includes the major inorganic reactions of chlorine and the reactions of chlorine atom with organic compounds. The reactions of chlorine are within the state of the science.